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ELASTOMERIC DITHIOPOLYESTERS

F. W. KNOBLOCH

MATERIALS LABORATORY

JUNE 1955

WRIGHT AIR DEVELOPMENT CENTER

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ELASTOMERIC DITHIOPOLYESTERS

F. W. KNOBLOCH

MATERIALS LABORATORY

JUNE 1955

PROJECT No. 7340

**WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO**

FOREWORD

This investigation was conducted by the Organic Materials Branch under Project No. 7340, "Rubber, Plastics, and Composite Materials", Task No. 73404, "Synthesis and Evaluation of New Polymers", formerly RDO No. 617-11, "Synthesis and Evaluation of New Polymers", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. Fred W. Knobloch acting as project engineer.

This report covers work conducted from 25 August 1954 to 20 October 1954.

ABSTRACT

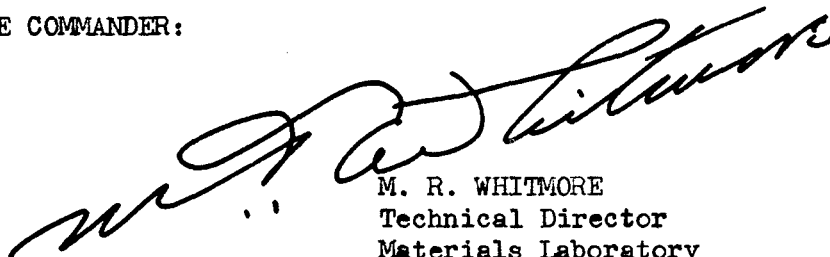
Elastomers have been prepared from an experimental liquid polymer formulation derived from a condensation product of mercaptoacetic acid and triethylene glycol. Two general types of these elastomers are discussed; one was obtained by reaction of the liquid polymer with organic and inorganic peroxides, the other by reaction of terminal mercapto groups with unsaturated aldehydes.

Selected specimens of each type of elastomer were successfully compounded and vulcanized using conventional rubber processing equipment. The behaviour of these vulcanizates in fuels and synthetic ester base oils has been studied along with the effects of aging at elevated temperatures. The vulcanized dithiopolyesters showed excellent resistance to the swelling action of 70/30 iso-octane/toluene fuel mixtures. Ester base oils of the MIL-L-7808A type were found to cause shrinkage. Elevated temperatures (350°F) consistently brought about rapid deterioration of both vulcanized and raw polymer stocks.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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I. INTRODUCTION

The Air Force's continuing search for elastomers with exceptional thermal stability combined with superior fuel and oil resistance has led to the investigation of many new polymers of novel chemical composition and structure (Ref. 1). This report describes studies relating to the development of one such experimental polymer belonging to the general class of dithiopolyesters.

The preparation of polyester elastomers has long been plagued with the progressive difficulty of forming new ester links as the chain length of the polymer increases. However, the development of the Vulcollan type rubbers (Ref. 2), which utilize diisocyanates to react with and extend the polymer chains, has provided a useful tool for the preparation of high molecular weight condensation polymers.

The present investigation involves a similar extension of the molecular weight which is accomplished by somewhat different approaches than are employed in the Vulcollan process. Some of these new elastomers were first prepared by the Coast Paint and Chemical Company* under Contract AF 33(600)-19202 (Ref. 3a). The present study is a continuation and expansion of the original contractual effort. The elastomers described herein all originated from condensation of 1 mole of triethylene glycol with 2 moles mercaptoacetic acid; the diester product was then oxidized with hydrogen peroxide and finally heat treated at 200-225°C for one and one half hours to yield an amber, viscous flowing oil. This oil was obtained from the Coast Paint and Chemical Company and is designated PE 26H.

In the present investigation, two methods were employed to convert the PE 26H polymer to elastomers. These methods are discussed under Section II and depend upon further reaction of terminal mercapto groups. The elastomers obtained by the first method are designated for convenience as the peroxide type; elastomers prepared by the second method are designated as the thioacetal type. Elastomeric products obtained were vulcanized and finally evaluated with respect to possible Air Force applications.

* Presently: The Coast Pro-Seal and Manufacturing Company
1507 Grande Vista Avenue
Los Angeles 23, California

II. RESULTS AND DISCUSSION

Preparation of Peroxide Type Elastomers

The possibility of increasing the molecular weight of the PE 26H polymer by oxidation of terminal mercapto groups with various peroxides was first investigated. Lead peroxide and benzoyl peroxide were found to be particularly effective for the conversion of liquid PE 26H to elastomeric products. On the other hand, elastomers prepared with hydrogen peroxide, when not further purified, reverted to viscous oils after standing at room temperature for approximately 12 hours. There were indications that PE 26H elastomers prepared with benzoyl peroxide were also slowly breaking down after standing at ambient temperatures for several months. Occurrences of similar polymer degradation have been reported with other peroxide-formed disulfides (Ref. 4); however, this phenomenon was never observed with raw stocks prepared with lead peroxide or with any vulcanized samples.

The polymers initially obtained by oxidation of PE 26H were soft and in all cases had low extensibilities. Further efforts were directed toward the preparation of raw polymers with improved elongations. Some degree of improvement was attained by reduction of the amount of peroxide employed. The most extensible polymers were produced with three parts of benzoyl peroxide per 100 parts of PE 26H. These observations and general reaction conditions are summarized in Table I. (Experimental details are presented in Section III.)

Vulcanization of Peroxide Type Elastomers

Like many new and unconventional rubbery polymers, the soft, tacky PE 26H peroxide elastomers initially presented serious processing difficulties. Preliminary compounding studies indicated that fillers such as CaCO_3 , Santocel-C*, and ZnO failed to give the polymer sufficient body for easy processing. Much improved handling characteristics were obtained with moderate carbon black loadings of between 40-50 parts per 100 parts of polymer.

All of the PE 26H peroxide elastomers adhered firmly to the mill rolls during compounding. Coating the rolls with a film of stearic acid prior to milling greatly facilitated the removal of the compounded

* Santocel-C: Monsanto Chemical Company.

TABLE I

PREPARATION OF PEROXIDE TYPE ELASTOMERS FROM LIQUID PE 26H

Reaction Number	Liquid PE 26H (Parts by Weight)	Oxidant (Parts by Weight)	Reaction Time (Minutes)	Reaction Temperature	Observations, Remarks, and Special Conditions
1	100	none	120	200-250°C	Reactants darkened slightly; no increase in viscosity.
2	100	10 PbO ₂	10	to 150°C	Reactants mixed at room temperature; rubbery by 150°C. Heating at 150°C produced white fumes; additional PbO ₂ resulted in an increased evolution of gas. Heating at 240°C - some apparent depolymerization or degradation.
3	100	7 Bz ₂ O ₂ *	20	80°C	Polymerization terminated when first elastomeric properties became evident.
4	100	5 Bz ₂ O ₂	20	100°C	Elastomer was quite "short".
5	100	6 Bz ₂ O ₂	20	50-100°C	Rubbery product heated at 71°C for 21 hrs. Only a slight further increase in viscosity noted.
6	100	20 Bz ₂ O ₂	1	100°C	Very rapid reaction resulting in a foamed rubber. Excess Bz ₂ O ₂ and benzoic acid removed by methanol washing. Did not degrade (See # 7)
7	100	20 Bz ₂ O ₂	15	25°C	Exothermic reaction, no gas evolution. Not washed with methanol. Degraded to a tacky viscous glob on standing several months.
8	100	3 ml. 30% H ₂ O ₂ 2 drops conc. NH ₄ OH	10	25°C	Reverted to viscous oil on standing over night.
9	100	3 ml. 30% H ₂ O ₂	25	25°C	Reverted to viscous oil on standing several days.
10	100	4.3 Bz ₂ O ₂	20	50-140°C	Rubber heated an additional 2 hours with stirring at 150°C. Better extensibility than previous samples.
11	100	3.8 Bz ₂ O ₂	20	50-135°C	Heated additional 4 hours at 125-150°C with stirring. Product similar to that of #10.
12	100	3.0 Bz ₂ O ₂	20	50-130°C	Heated additional 2 hours at 125-150°C. Product more extensible than that of #10

* Benzoyl Peroxide

rubber; nevertheless, except when PbO_2 was employed, the uncured rubber compounds could only be removed from the mill rolls by scraping. In milling samples compounded with PbO_2 , the handling characteristics were found to be greatly improved; this was attributed to rapid reaction of the lead peroxide and partial curing of the rubber during milling operations. Various substances are known which can be used to retard such precuring (Ref. 3b) but investigations in this area were not undertaken.

Initial vulcanization studies sought to cure the PE 26H elastomers with residual peroxides which presumably were present in the rubber (see Table II). Consequently, no additional curing agent was used in these studies. Although this proved largely ineffective at molding temperatures, it is considered significant that compounded stocks left at room temperature showed evidence of some curing after a period of two hours (this was especially apparent when the stock contained carbon black fillers).

Blowing, or gas bubble formation in the molded compounds, was frequently observed. It could generally be eliminated by employing lower molding temperatures but even vulcanized samples were found to blow considerably if heat aged at $350^\circ F$ for as little as one hour.

Table II presents data and observations of interest in connection with the compounding of these polymers.

Several of the rubber compounds listed in Table II exhibited good elongation, flexibility and tensile strength combined with excellent resistance to fuels and oils at room temperature. However, one serious shortcoming soon became apparent; the elastomers hardened quite rapidly at elevated temperatures. It was obvious that the heat susceptibility of these PE 26H-peroxide type elastomers would have to be greatly improved before they could be considered to possess a definite potential for use in Air Force applications.

It has been found that the most effective curing systems for the peroxide derivatives of PE 26H involved the use of PbO_2 . The use of this metallic oxide, however, was suspected of being one of the factors contributing to the thermal sensitivity of the resulting vulcanizates. Other independent investigations by the Materials Laboratory have indicated that with certain amine cured acrylates, the incorporation of metallic oxides in the curing recipe resulted in products of lower thermal stability than were otherwise obtained. In addition, it has been pointed out that in analogous cures accomplished with Thiokol-type polymers, the following steps are involved (Ref. 5):

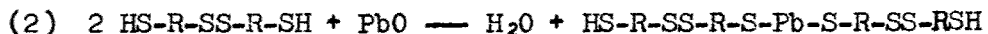
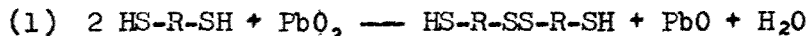


TABLE II

VULCANIZATION OF PEROXIDE TYPE ELASTOMERS

Reaction Sample Number	Sample Number	Filler (Parts by Weight)	Addi. Curing Agent (Parts by Weight)	Other Ingredients	Time (Minutes)	Temp. °F	Remarks
1	2	45 CaCO ₃ 10 HAF	none	TP 90B plasticizer	20	260	Weak rubber, appeared somewhat porous
2	2	45 CaCO ₃ 10 HAF	none	TP 90B plasticizer	20	310	Sample "blew" badly; otherwise good cure
3	3	60-Santocel-C	none	-	20	310	No elastic properties, soft, crumbled readily
4	4	40 Santocel-C	none	-	20	310	No appreciable cure, gray discoloration
5	4	40 Santocel-C	3 Bz ₂ O ₂	-	20	310	Gummy, slight cure (unmolded sample of this material cured appreciably in 2 hrs. at room temperature.)
6	5	20 SRF	none	-	20	310	Molding decreased viscosity of all samples. Compounds
7	5	30 SRF	none	-	20	260	molded at 260°F were "blown"
8	5	40 SRF	none	-	20	310	slightly; badly at 310°F. 40-
9	5	50 SRF	none	-	20	260	50 parts SRF seemed to be optimum loading. Unmolded
10	5	60 SRF	none	-	20	310	specimens cured considerably on
11	5	70 SRF	none	-	20	260	standing at room temperature for several hours.
12	6	50 SRF	3 PbO ₂	-	20	350	Severely blown; precured
13	6	50 SRF	3 PbO ₂	-	20	330	Very slight blowing; precured
14	6	50 SRF	3 PbO ₂	-	20	310	No blowing; precured
15	6	50 SRF	3 PbO ₂	-	20	300	No blowing; precured
16	7	50 ZnO	none	-	20	240	No cure; depolymerization
17	7	50 ZnO	none	-	20	310	No cure; depolymerization
18	10	40 SRF	3 PbO ₂	-	20	310	Badly blown
19	10	40 SRF	3 PbO ₂	-	20	240	Very good sample
20	11	50 HAF	3 PbO ₂	Stearic acid on mill rolls	20	240	Very good sample
21	12	50 HAF	3 PbO ₂	Stearic acid on mill rolls	25	240	Very good sample

Note: Sample Number above is identical with "Reaction Number" in Table I; 100 parts by weight of polymer were used in all cures.

HAF - High abrasion furnace black; Santocel-C - Monsanto Chemical Co.; SRF - Semireinforced furnace black; TP 90B - Thiokol Corporation

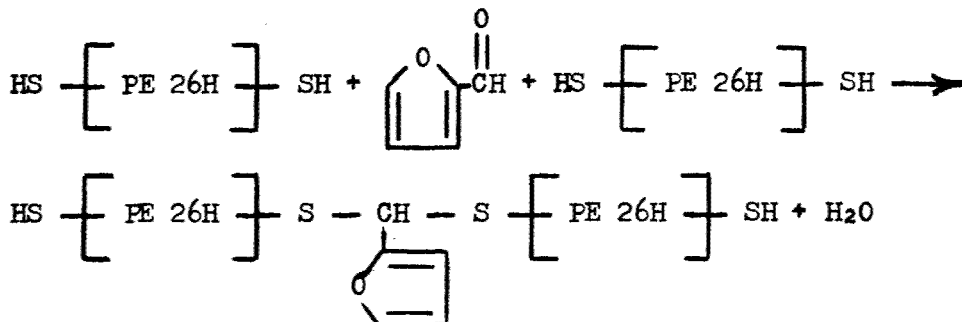
At temperatures as low as 250°F, lead sulfide was found to slowly split from the chain. Subsequent elastomer preparations attempted to eliminate the use of PbO₂ and the further formation of disulfide linkages.

Preparation of Thioacetal Type Elastomers

The liquid PE 26H polymer was also converted to elastomeric materials of interest by reaction of terminal mercapto groups with unsaturated aldehydes in the presence of acid catalysts.

A complex series of competing reactions with the reactants under consideration was realized. These included addition of mercapto groups across unsaturated groups of the aldehydes, homopolymerization of aldehydes in the presence of strong acids and the desired thioacetal formation. Elucidation of the reaction or reactions which occurred was beyond the scope of the present investigation and it was presumed the reaction was mainly that of thioacetal formation. This presumption was not without some basis, however, since Marvel *et al* have recently described the HCl-catalyzed preparation of polythioacetals (Ref. 6), and Holmberg has reported the preparation of mercaptals (thioacetals) from cinnamaldehyde and 2-furaldehyde using conc. HCl as a catalyst (Ref. 7). Szabo and Stiller have also reported the preparation of cinnamaldehyde dibenzyl mercaptal from the corresponding aldehyde and mercaptan (Ref. 8).

The desired thioacetal reaction is outlined below:



Elastomers were readily produced by this method using several aldehydes, namely 2-furaldehyde, cinnamaldehyde, and crotonaldehyde (See Table III). Unsaturated aldehydes were selected because of the probable value of their unsaturation in connection with vulcanization reactions.

The first elastomers of this series were prepared by reacting PE 26H with 2-furaldehyde. Catalytic amounts of ferric chloride were found to effectively promote the reaction. Likewise elastomers were readily

formed when small amounts of concentrated hydrochloric acid were employed. A reaction also progressed, although much more slowly, in the absence of added catalyst.

Table III summarizes the preparation of elastomers of this thioacetal type from liquid PE 26 H polymer.

Vulcanization of Thioacetal Type Elastomers

The presence of unsaturated groups in these polymers appeared to have little if any effect on cures with benzoyl peroxide; some cure was noted with a sulfur recipe but the cured stock cracked and broke readily upon flexing. It was found necessary to revert back to PbO_2 to induce a final cure during molding; exceptionally good elastomers resulted which appeared to be superior to all other elastomers produced in this investigation. Pertinent compounding and vulcanization data are provided in Table IV.

Oven aging at $105^\circ C$ resulted in a decrease in viscosity of the uncompounded thioacetal type elastomers. The cause of this was not determined but it will be recalled that a similar situation was encountered with some of the peroxide prepared elastomers and was found to occur in some cases even at room temperature.

Evaluation Studies with Dithiopolyester Elastomers

Physical Data. The vulcanized PE 26H elastomers, particularly those prepared with aldehydes, compared very well in "feel" to other common rubbers. The tensile strengths, although quite low, could presumably be improved with a more intensive compounding study than was undertaken in connection with this investigation. Finer blacks, for example, were found to increase tensiles considerably. Representative physical data obtained with two of the best experimental peroxide type polymers are presented in Table V.

Resistance of these compounds to the swelling action of 70/30 iso-octane/toluene fuel mixtures was excellent. Also, in synthetic diester base engine oils (MIL-L-7808A), the expected large swell of the ester rubber was not realized--on the contrary, considerable shrinkage was in evidence. Table VI summarizes swelling data obtained with these peroxide type PE 26H elastomers.

Thermal Stability. The most obvious shortcoming of both the PE 26H peroxide and the thioacetal type of elastomers was their decided lack of thermal stability. Their weight loss on heat aging

TABLE III

PREPARATION OF THIOACETAL TYPE ELASTOMERS FROM LIQUID PE 26H

Reaction No.	Liquid PE 26H (Parts by Weight)	Aldehyde and Catalyst (Parts by Weight)	Reaction Temperature (°C)	Remarks
1A	100	FeCl ₃ - trace	120	No elastomer formed; skin on surface of liquid PE 26H
2A	100	15 Furfural Trace FeCl ₃	25	Reaction only required a few minutes. Soft, weak rubber produced; possessed poor resiliency
3A	100	15 Furfural Trace HCl	25	Soft, weak rubber; possessed poor resiliency
4A	100	15 Furfural No catalyst	25	Similar to elastomer obtained in Runs 1A and 2A; Reaction time was considerably longer
5A	100	10 Cinnamaldehyde Trace FeCl ₃	120	Reaction began immediately upon addition of FeCl ₃
6A	100	10 Cinnamaldehyde Trace FeCl ₃	120	FeCl ₃ was dissolved in aldehyde for better dispersion. Reacted immediately upon addition to liquid PE 26H. Heating 1 hour at 105°C caused a decrease in viscosity.
7A	100	10 Cinnamaldehyde Trace HCl	150	Rapidly converted to an elastomer upon addition of HCl. Heated 1 hr. at 105°C; some decrease in viscosity resulted.
8A	100	10 Cinnamaldehyde Trace HCl	150	Aranox* antioxidant (30 parts) was dissolved in PE 26H. Product was elastomeric after 1 hour.
9A	100	10 Crotonaldehyde Trace HCl	120	Elastomeric product obtained after 1 hour of heating.

* Aranox - Naugatuck Chemical Co.

TABLE IV

VULCANIZATION OF THIOACETAL TYPE ELASTOMERS

Reaction No.	Sample* (100 parts)	Filler (Parts by Weight)	Curing Agent Other Than Residual Aldehyde (Pts by Wt)	Other Ingredients (Parts by Weight)	Time (Min.)	Temp. (°F)	Remarks
1	4A	60 HAF	none	-	60	250	Soft cure
2	2A	60 HAF	2PbO ₂	3 Stearic Acid	60	260	Soft; low elongation appeared undercured.
3	8A	50 Santocel-C	3 Bz ₂ O ₂	-	30	250	Soft, no cure
4	8A	75 Santocel-C	10 Bz ₂ O ₂	-	30	310	Soft, no cure
5	8A	75 Santocel-C	20 Bz ₂ O ₂	-	30	310	Soft; no cure
6	7A	50 HAF 5 ZnO	1 Tuads 2 Sulfur	1 Telurack 1.5 Stearic Acid	60	260	Cured; broke on 180° flex.
7	9A	50 HAF	3 PbO ₂	2 Stearic Acid	30	240	Produced best rubber in this series.
8	2A	50 HAF	2 PbO ₂	3 Stearic Acid	60	260	Good rubber obtained. Pre-cured somewhat prior to molding.

* Sample identification same as in Table III
 Tuads - R. T. Vanderbilt Company
 Telurack - R. T. Vanderbilt Company

TABLE V
PROPERTIES OF COMPOUNDED PE 26H PEROXIDE TYPE ELASTOMERS

<u>Sample Number*</u>	<u>Modulus at 100% Elongation (psi)</u>	<u>Elongation at Break %</u>	<u>Tensile (psi)</u>	<u>Permanent Set %</u>	<u>Shore Durometer Hardness A - Scale</u>
21	405	187	575	5	-
21	425	181	628	5	-
21	349	193	732	-	57
19	548	175	1017	3	-
19	660	173	990	4	-
19	504	180	988	-	-

* Same as "Reaction Number" in Table II

TABLE VI
VOLUME CHANGE OF COMPOUNDED PEROXIDE TYPE
ELASTOMERS IN FUELS AND OILS

<u>Sample Number*</u>	<u>Fluid</u>	<u>Temperature (°F)</u>	<u>Time (hours)</u>	<u>Swell (%)</u>	<u>Remarks</u>
20	70/30 Iso- octane/Toluene	68	90	6.1	Retained physical properties
21	70/30 Iso- octane/Toluene	68	48	5.8	Retained physical properties
20	MLL-L-7808A (diester base oil)	68	48	-1.3	Retained physical properties
20	MLL-L-7808A	350	24	-12.4	Hard

* Identical with "Reaction Number" of Table II

at 300°F was appreciable, and as shown in Figure 1, the compounded stocks investigated were considerably worse in this respect than the uncompounded. The observed weight loss at 400°F was particularly severe.

Aging in air for as little as four hours at 300°F caused the compounded stocks to become leather-like and crack on flexing. Samples aged for 90 hours at 300°F had increased in hardness to such an extent that a measurement could not be obtained with a Shore A Durometer. However, the aged polymers, although hard and nonflexible, could be struck a fairly sharp blow with a hammer without being crushed.

The elastomers obtained by reaction of liquid PE 26H polymer with various unsaturated aldehydes also exhibited poor thermal stability; like the peroxide type elastomers, they hardened rapidly when air aged at elevated temperatures. Representative results comparing the increase in hardness on heat aging of the two types of elastomers are presented in Table VII.

FIGURE I.
AIR AGING OF PE 26H POLYMERS AT 300°F

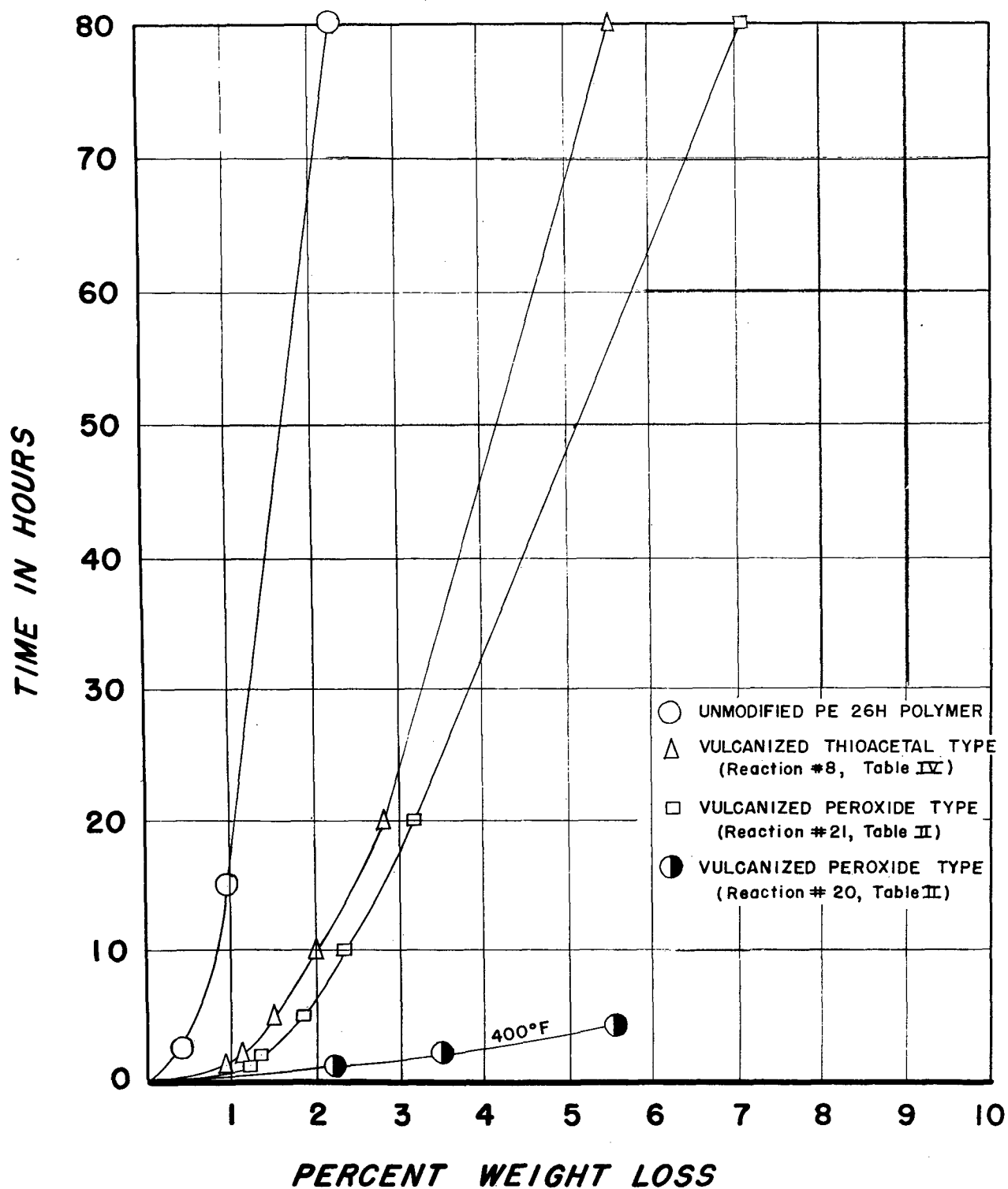


TABLE VII
HARDENING OF TYPICAL PE 26H ELASTOMERS ON HEAT AGING
(SHORE A DUROMETER HARDNESS)

<u>Sample</u>	<u>Initial Hardness</u>	<u>After 1 hr. at 350°F</u>	<u>After 3 hrs. at 300°F plus 1 hr. at 350°F</u>	<u>After 12 hrs. at 300°F plus 1 hr. at 350°F</u>
Thioacetal Type Elastomer (Reaction 7 Table IV)	65	63	75	85
Peroxide Type Elastomer (Reaction 21 Table II)	50	58	70	82

III. EXPERIMENTAL PROCEDURES

Typical procedures for preparing and vulcanizing the modified PE 26H polymers are presented below:

Preparation of the Peroxide Type Elastomer

To a 30 ml. beaker equipped with a power stirrer, 10.0 gm. of liquid PE 26H polymer were added. Finely powdered benzoyl peroxide (0.30 gm.) was then added and thoroughly dispersed by stirring at room temperature. The mixture was then slowly heated, with continued stirring, to 130°C. As the viscosity of the reaction mixture increased, stirring became ineffective due to the adherence of polymer to the stirrer. The polymer was removed to a Petri dish (where it could be mixed by hand) and the heating continued on a hot plate for two hours at 125-150°C. A tacky elastomer having fair elongation was obtained as a typical product.

Vulcanization of the Peroxide Type Elastomer

Compounding was accomplished on a small 1 $\frac{1}{4}$ inch rubber mill. The rolls were coated with stearic acid to lessen adherence of the elastomer. The polymer (100 parts) was milled with 50 parts of HAF (Philblack O). Lead peroxide (3 parts) was then gradually added. Some precuring was in evidence which improved milling characteristics and allowed the polymer to be sheeted from the rolls.

Molding and vulcanization were accomplished in a press cure at 240°F for 25 minutes.

Preparation of the Thioacetal Type Elastomer

To 3.0 gm. of liquid PE 26H polymer in a 30 ml. beaker equipped with stirrer, 0.3 gm. of crotonaldehyde was added. The mixture was heated with stirring to 150°C.

A stirring rod wet with concentrated HCl was momentarily injected into the agitated mass. The reaction mixture was converted to an elastomer in several minutes.

Vulcanization of the Thioacetal Type Elastomer

To 100 parts of polymer, two parts HAF (Philblack-0) were added during milling. Lead peroxide (3 parts) was then introduced with continued milling. The compounded stock handled as easily as conventional rubbers at this stage, banding and sheeting readily. Molding and vulcanization were accomplished simultaneously in a press cure at 240°F for 30 minutes.

IV. CONCLUSIONS

This investigation has demonstrated that elastomeric dithiopolyesters can be quite readily handled with conventional rubber processing equipment and can be vulcanized to yield interesting rubber compounds. Exceptional resistance to the swelling action of 70/30 iso-octane toluene fuel mixtures was exhibited by the vulcanized dithiopolyesters. All of the elastomers exhibited poor thermal stability in various environments at 350°F.

Attempts to improve the thermal stability of the dithiopolyesters without substantially changing the base polymer formulation would appear likely to yield at most only marginal improvements. Further study of these dithiopolyester systems would probably contribute most to the ultimate development of useful elastomers if such study were directed towards elucidation of the specific nature of their thermal degradation.

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